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#### (54) Title: CROSS-LINKABLE PERMANENT SURFACE TREATMENT AGENTS

### (57) Abstract

An antistatic composition containing (a) a cross-linked thermosetting resin formed by reacting, in the presence of a water-soluble solvent, a polyaminoamide having unreacted primary and secondary amine groups and an anhydride selected from the group consisting of dianhydride, maleic anhydride, and mixtures thereof, and (b) a cationic polymer.

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## CROSS-LINKABLE PERMANENT SURFACE TREATMENT AGENTS

## Field of the Invention

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The present invention generally relates to an antistatic composition for polymeric materials. More
particularly, by cross-linking a polyalkylenepolyamine with
maleic anhydride, and then blending the cross-linked
product with a cationic complexing agent, an anti-static
composition is formed which, when applied onto a polymeric
substrate permanently imparts enhanced surface properties;
onto the substrate.

## 10 Background of the Invention

The production of static electricity on polymeric materials caused by the accumulation of electrical charge thereon creates problems. Both natural and synthetic polymeric fibers have a tendency to accumulate electrical charge, resulting in the production of static electricity.

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Numerous methods have been proposed to prevent such electrification. Examples include the application of a surfactant having antistatic properties onto the surfaces of polymeric fibers. The antistatic effects of such surfactants, however, has proven to be only temporary due to their lack of durability. Anti-stat properties can be lost during the dyeing process, or during cleaning or by The second section of the second seco antistatic agent be incorporated directly into a polymeric fiber during its formation, while at the same time attempting to maintain the fiber's spinnability and quality of construction.

It is common knowledge that fibers prepared from conventional natural and synthetic polymeric materials tend to collect and retain, for periods of time, static electrical charges when coming into contact with each other or foreign objects. The electrostatic charge build-up can occur quite rapidly and often dissipation of the charge into the environmental atmosphere is extremely slow. consequence of this is that the polymeric material may remain electrostatically charged for hours at a time. This property tends to make filaments difficult to handle during manufacturing operations and results in objectionable fiber properties, particularly in wearing apparel and carpeting. 25. Electrostatically charged polymeric textile materials may y grannot, only attract each other, but may also attract such things as dust, dirt, and lint.

The accumulation of static charges and the slow

dissipation thereof on polyamide fibers prevents finished, polymeric fabrics from draping and wearing in a desirable manner, and causes the same to cling uncomfortably to the body of the person wearing them. Fibers having a high electrostatic susceptibility often cling to guides and rolls in textile machinery during the manufacturing and processing thereof and are sometimes seriously damaged and weakened. As a result, the quality of the end product is lower than it might otherwise be. For these reasons, and because end-uses such as garments, upolstery, hosiery, rugs, blankets and fabrics are greatly benefited by a reduced tendency to accumulate and maintain electrostatic charges, a permanent antistatic composition to be applied thereon is highly desirable.

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Presently, in the commercial production of natural and synthetic polymeric fibers, the as-spun filaments are given some treatment to improve their electrostatic and handling properties. This treatment usually consists of passing the filaments, while in the form of a bundle, through a bath or over a wheel coated with a treating of finishing liquid. The finish thus applied is a coating and is not of a permanent nature. Most, if not all, of the antistatic agent on the fiber surface is lost in subsequent processing of the filament by mechanical handling, heating, washing, scouring and dyeing. If the antistatic agent does remain on the fiber until the final end product is produced, it often becomes less effective after the end product is used for a period of time, and especially after a number of

washings or dry cleaning operations.

permanent antistatic polymeric fibers and articles by the application of a more permanent coating. However, due to the harsh finishing applications the coated fibers were subsequently exposed to, the coatings would either be removed and/or fail to perform adequately. It has also been attempted to incorporate hydrophilic antistatic type comonomers directly into the base polymeric materials. For various reasons, however, such as a resulting harsh fiber surface or sacrifice of good fiber physical properties, these methods have been proven unsuccessful.

Antistatic compositions are also used for enhancing the receptivity of plastic surfaces to electrostatically applied coatings, e.g., in automobile production. In this application it is also desirable that the antistatic composition resist removal when exposed to an aqueous rinse or wash liquid.

Accordingly, it is a primary object of the present invention to provide novel compounds capable of dissipating electrical charges.

Another object of the invention is to provide a process for imparting permanent antistatic properties onto natural and synthetic polymeric materials.

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# 25 <u>Summary of the Invention</u>

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The present invention is directed to a new and novel antistatic composition capable of being permanently affixed

to a polymeric material, the antistatic composition containing (a) a crosslinked thermosetting resin formed by reacting, in the presence of a water-soluble solvent, a polyaminoamide having unreacted primary and secondary amine groups and an anhydride selected from the group consisting of dianhydride, maleic anhydride, and mixtures thereof, and (b) a cationic polymer.

There is also provided a process for producing an antistatic composition involving the steps of (a) forming a polyaminoamide having unreacted primary and secondary amine groups, (b) reacting, in the presence of a water-soluble solvent, said polyaminoamide with an anhydride selected from the group consisting of dianhydride, maleic anhydride, and mixtures thereof, to form a crosslinked thermosetting resin, and (c) blending said crosslinked thermosetting resin with a cationic polymer.

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The present invention also provides a process for permanently affixing an antistatic composition onto a natural and synthetic polymeric substrate comprising contacting said substrate with an antistatic composition containing (a) a crosslinked thermosetting resin formed by reacting, in the presence of a water-soluble solvent, a polyaminoamide having unreacted primary and secondary amine groups and an anhydride selected from the group consisting of dianhydride, maleic anhydride, and mixtures thereof, and (b) a cationic polymer.

are also useful for imparting a desired level of surface

conductivity onto formed plastic articles, such as automobile bumper parts, for electrostatically applied coating materials, resulting in good adhesion of the coating material onto the treated article.

## Description of the Invention

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Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as being modified in all instances by the term "about".

The composition of the present invention is formed by blending into a crosslinked thermosetting resin a cationic polymer. The crosslinked thermosetting resin is first formed by reacting a polyaminoamide with an anhydride.

The polyaminoamide of the present invention is preferably formed by reacting a polyamine with a polyacid. The amine groups of the polyamine are primary and/or secondary amine functional groups and can be present as part of the polymer backbone, polymer endgroups or pendent branches to the main polymer chain. Suitable polyamines include, for example, diethylenetriamine, triethylenetetramine and tetraethylenepentamine. Particularly preferred polyamines are diethylenetriamine and triethylenetetramine.

Suitable polyacids include, for example, malonic acid, succinic acid, glutaric acid, adipic acid and sebacic acid.

A particularly preferred polyacid is adipic acid.

Thus, by reacting a polyamine with a polyacid, a

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suitable polyaminoamide may be formed. Optionally, reactants such as  $C_{36}$  dimer and  $C_{54}$  trimer acids, methyl esters of fatty alcohol ethoxylates (oxa-acids), amine terminated EO homopolymers or EO-PO block copolymers (JEFFAMINES® supplied by Huntsman Corporation) can be added in amounts of up to 50% by weight on reactants. Other useful polymers which may also optionally be added include polyethylenimine, poly-N-vinylamine, polyallylamine, polydiallylamine, copolymers of polyvinylalcoholvinylamine, and vinyl addition copolymers containing polyallylamine or polydiallylamine functionalities.

Another option which may be exercised in the formation of the polyaminoamide resin is reacting up to about 10% of the primary and secondary amines in the polyaminoamide resin with mono-chlorohydrin derivatives. The monochlorohydrin derivatives which may be used include C6-20 fatty ethoxylates and/or propoxylates or EO-PO random block coolymers thereof having from at least 1 up to about 200 moles alkoxylate reacted with fatty alcohol in which the ratio of ethylene oxide to propylene oxide is in the range from about 25 : 1 to about 4 : 1, respectively, to produce a modified polymer containing primary and secondary amine functionalities and fatty alkoxylate pendent groups. The mono-chorohydrin derivatives are prepared by reacting epichlorohydrin with an alkoxylated fatty alcohol of choice at equal molar ratios using a boron trifluoride catalyst. The incorporation of these hydrophobic mono-chlorohydrin derivatives into the polyaminoamide resin helps to

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establish permanence of the antistat composition onto the polymeric material.

The polyaminoamide resin is then reacted with an anhydride selected from a dianhydride, maleic anhydride or combination thereof. The crosslinking reaction is conducted in a solvent, at a reaction temperature of from about 25 to 100°C, preferably from about 50 to 100°C, and most preferably from about 60 to 80°. Suitable solvents include, for example, water or water soluble solvents such as ethylene glycol, diethylene glycol, propylene glycol, and the like.

The polyaminoamide is reacted with the anhydride at a mole ratio of anhydride: unreacted amine groups of from about 0.1: 1.0 to form the crosslinked thermosetting resin. The reaction is allowed to proceed until all of the anhydride has reacted with the unreacted amine groups of the polyaminoamide and a solution viscosity at about 35% solids of at least about 300 cps at 25°C, as measured using a Brookfield Viscometer, is achieved. The crosslinked thermosetting resin thus formed is then stabilized by adjusting the solution pH to less than 9 with acid.

The concentration of the polyaminoamide and anhydride reactants in the solvent is from about 0.1 to 60% by weight, preferably from about 25 to 40% by weight, and most preferably about 35% by weight, all weights being based on the weight of the crosslinked thermosetting resin.

Once the crosslinked thermosetting resin is formed, a cationic polymer is added thereto, thus forming the

permanent antistatic composition of the present invention. From about 1 to about 25% by weight, based on the weight of the crosslinked thermosetting resin, of a cationic polymer is blended with the crosslinked thermosetting resin. 5 Suitable cationic polymers include, for example, polydiallyldimethylammonium chloride and its copolymers, homo- and co-polymers based on polymerizing quaternary monomers such as dimethyl or diethyl aminoethylacrylate dimethylsulfate or dimethylchloride, dimethyl or diethyl 10 aminoethylmethacrylate dimethylsulfate or dimethylchloride, dimethylaminopropylmethacrylamide dimethylchloride, and the like.

The present invention also provides a process for antistatic composition capable of making an permanently affixed onto a natural or synthetic polymeric textile substrate. The process involves reacting the above-disclosed polyaminoamide and anhydride to form the crosslinked thermosetting resin, the conditions per disclosed above. A cationic polymer is then blended with crosslinked thermosetting resin, also per conditions disclosed above, to form the composition of the present invention.

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There is also provided a process for permanently treating a natural and synthetic polymeric substrate with an antistatic composition involving contacting the substrate with the antistatic composition of the invention. Polymeric substrates onto which the antistatic composition of the present invention may be applied include, for

examples, nylon (polyamide), polycarbonate, polyphenylene oxide, polyester, polyolefins and the like, as well as blends thereof with various other compatible resins.

The composition and process of the present invention may also be employed to dissipate an electrostatic sharge on a static prone natural or synthetic polymeric substrate, thereby imparting a desired level of surface conductivity onto formed articles of manufacture such as, for example, various automobile parts. Permanent surface conductivity can be provided in either of two ways. contacting the exterior surfaces of the already formed , articles of manufacture with the antistatic composition of the present invention. The other is by blending from about 0.1 to about 10% by weight, based on the weight of the hot melt polymeric substrate, of the antistatic composition with the hot melt substrate used to make the article of manufacture prior to its being formed (cast). The finished article of manufacture thus contains the antistatic composition dispersed throughout its matrix.

The present invention will be better understood from the examples which follow, all of which are intended to be illustrative only and not meant to unduly limit the scope of the invention. Unless otherwise indicated, percentages are on a weight-by-weight basis.

# 25 I. Preparation of Polyaminoamide resin

# Example A . It was to be a factor of the contract of the contr

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To a resin reactor was charged one mole of a dibasic of

acid ester mixture containing 65% dimethyl glutarate and 35% dimethyl adipate and one mole of diethylenetriamine. Stirring and nitrogen sparge was started with the contents of the reactor being heated to about 150°C - 160°C. Methanol started to reflux in the reactor at about 157°C. The reflux was allowed to continue until the reaction temperature reached about 85°C, at which time the methanol was distilled off. The reaction temperature was maintained at about 150°C - 160°C for approximately 3 hours, the time required for distillation of about 85% of the theoretical amount of methanol. The Brookfield viscosity (spindle #2 at 30 rpm at 25°C) of a 48.4% aqueous solution of the resin thus obtained was 705 cps. The pH of the resin solution was about 10.0. The total alkalinity of the resin solution . was 133.8 mg KOH/gram.

## Example B

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acid ester mixture containing 65% dimethyl glutarate and 35% dimethyl adipate, 0.07 moles of EMPOL® 1008, a C<sub>36</sub> dimer acid available from Henkel Corp., and 3.78 moles of diethylenetriamine. Stirring and nitrogen sparge was started with the contents of the reactor being heated to about 170°C. Methanol started to reflux in the reactor at about 146°C, and was collected as it distilled off. Once the reactants reached a temperature of 177°C, the reaction contents were allowed to react until about 98% of the theoretical amount of methanol was removed by distillation.

The Brookfield viscosity (spindle #2 at 30 rpm at 25°C) of a 34.7% aqueous solution of the resin thus obtained was 147 cps. The pH of the resin solution was about 9.8. The total alkalinity of the resin solution was 94.76 mg KOH/gram.

## Example C

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To a resin reactor was charged 3.71 moles of a dibasic acid ester mixture containing 65% dimethyl glutarate, 35% dimethyl adipate, 0.07 moles of Empol® 1008, 2.83 moles of diethylene triamine, and 0.94 moles JEFFAMINE® EDR-192, a polyethylenoxide diamine having 4 moles of ethylene oxide, available from Huntsman Corporation. Stirring and nitrogen sparge was started with the contents of the reactor being heated to about 177°C. Methanol started to reflux in the reactor at about 139°C, and was collected as it distilled off. Once the temperature of the reactants reached 177°C, the reaction contents were allowed to react until about 94% of the theoretical amount of methanol was removed by distillation. The Brookfield viscosity (spindle #2 at 30 rpm at 25°C) of a 50.7% aqueous solution of the resin thus obtained was 2,440 cps. The pH of the resin solution was about 10.2. The total alkalinity of the resin solution was 99.00 mg KOH/gram.

# II. Preparation of Mono-Chlorohydrin Derivatives

### 25 <u>Example D</u>

To a reaction flask were charged 100.0 grams of NEODOL® 25-12 (a mixture of  $C_{12-15}$  linear alcohols

ethoxylated with 12 moles of ethylene oxide, available from Shell Chemical Company), and 60 grams of toluene. The contents in the flask were heated to reflux (about 124°C) with moisture being distilled off. After removing about 22.1 grams of azeotrope (water-toluene mixture), the reaction contents were cooled to about 40°C. 0.8 grams of boron trifluoride-acetic acid complex and 12.7 grams of epichlorohydrin were then added to the reaction flask. The reaction contents were then heated to 70°C and held at this temperature until all the epichlorohydrin was reacted. 2.5 grams of a 50% aqueous sodium hydroxide solution was then added with the remaining toluene being distilled off at 150°C. The reaction product was then filtered to remove insoluble salts while hot. The active chlorine in the product was calculated to be 4.3%.

#### Example E

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To a reaction flask were charged 100.0 gram of TRYCOL® 5954, a lauryl alcohol ethoxylated with 23 moles of ethylene oxide, available from Henkel Corp., Emery Division, and 60 grams of toluene. The contents in the flask were then heated to reflux (about 124°C) with moisture being distilled off. After removing about 22.3 grams of azeotrope (water-toluene mixture), the reaction contents were then cooled to about 40°C. To the reaction flask were then added 0.8 grams of boron trifluoride-acetic acid complex and 7.7 grams of epichlorohydrin. The reaction contents were then heated to 70°C and held at this

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temperature until all of the epichlorohydrin was reacted.

2.5 grams of a 50% active solution of sodium hydroxide was then added, with the remaining toluene being distilled off at 150°C. The reaction product was then filtered to remove insoluble salts while hot. The active chlorine in the product was calculated to be 2.7%.

# Example F

To a reaction flask were charged 100.0 grams of TERGITOL®-15-S-40, a mixture of C<sub>11-15</sub> linear alcohols ethoxylated to 40 moles of ethylene oxide, available from Union Carbide, and 60 grams of toluene. The contents in the flask were heated to reflux (about 124°C) and moisture was distilled off. After removing about 22.2 grams of azeotrope (water-toluene mixture), the reaction contents were then cooled to about 40°C. To the reaction flask were then added 0.8 grams of boron trifluoride-acetic acid complex and 4.7 grams of epichlorohydrin. The reaction contents were heated to 70°C and held at this temperature until all of the epichlorohydrin was reacted. 2.5 grams of a 50% active aqueous sodium hydroxide solution was then added, and the remaining toluene was distilled off at 150°C. The reaction product was then filtered to remove insoluble salts while hot. The active chlorine in the product was calculated to be 1.72%.

# 25 III. <u>Preparation of Crosslinked Resins</u>

# Example 1

To a resin reactor were charged 116.4 grams of the polyaminoamide resin of Example A and 22.8 grams of the mono-chlorohydrin of Example D. The reactor contents were heated to 80°C and held at this temperature until the total alkalinity of the solution was about 101.7 mgKOH/gram. polyaminoamide resin reaction product was diluted with 109.5 grams of water and cooled to about 60°C. anhydride in the amount of 12.2 grams was then added and allowed to react at about 80°C until a Brookfield viscosity of 1075 cps (spindle #2 at 12 rpm at 25°C) was obtained. After which, 117.9 grams of water and 22.8 grams of a 40% aqueous solution of polydimethydiallylammonium chloride were added, followed by adjusting the pH of the aqueous resin solution to 4.0 with 96% sulfuric acid. The resulting resin solution had a Brookfield viscosity of 232 cps (spindle #2 at 30 rpm at 25°C), a pH of 4.0, and a solids content of 23.1%.

#### Example 2

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To a resin reactor were charged 116.4 grams of the polyaminoamide resin of Example A and 11.4 grams of the mono-chlorohydrin of Example D. The reactor contents were heated to 80°C and held at this temperature until the total alkalinity of the solution was about 113.5 mgKOH/gram. The polyaminoamide resin reaction product was diluted with 89.6 grams of water and cooled to about 60°C. Maleic anhydride in the amount of 12.9 grams was then added and allowed to react at about 80°C until a Brookfield viscosity of 1565

cps (spindle #2 at 12 rpm at 25°C) was obtained. After which, 102.2 grams of water and 20.3 grams of a 40% aqueous solution of polydimethydiallylammonium chloride were added, followed by adjusting the pH of the aqueous resin solution to 4.0 with 96% sulfuric acid. The resulting resin solution had a Brookfield viscosity of 332.5 cps (spindle #2 at 30 rpm at 25°C), a pH of 4.0, and a solids content of 25.2%.

## Example 3

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To a resin reactor were charged 122.9 grams of the polyaminoamide resin of Example A and 18.9 grams of the mono-chlorohydrin of Example E. The reactor contents were then heated to 80°C and held at this temperature until the alkalinity of the solution was about total mgKOH/gram. The polyaminoamide resin reaction product was then diluted with 107.5 grams of water and cooled to about Maleic anhydride in the amount of 13.6 grams was then added and allowed to react at about 80°C until a Brookfield viscosity of 1762.5 cps (spindle #2 at 12 rpm at 25°C) was obtained. After which, 116.9 grams of water and 40% aqueous solution grams of a polydimethydiallylammonium chloride were added, followed by adjusting the pH of the aqueous resin solution to 4.0 with 96% sulfuric acid. The resulting resin solution had a 25 Brookfield viscosity of 290.0 cps (spindle #2 at 30 rpm at 25°C), a pH of 4.0, and a solids content of 26.0%.

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#### Example 4

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The procedure of Example 3 was repeated, the difference being that this time 11.5 grams of a 40% aqueous solution of polydimethydiallylammonium chloride was added to the resin solution prior to the pH adjustment with sulfuric acid. The resulting resin solution had a Brookfield viscosity of 295.0 cps (spindle #2 at 30 rpm at 25°C), a pH of 3.1, and a solids content of 24.7%.

#### Example 5

The procedure of Example 3 was repeated, the difference being that this time 34.5 grams of a 40% aqueous solution of polydimethydiallylammonium chloride was added to the resin solution prior to the pH adjustment with sulfuric acid. The resulting resin solution had a Brookfield viscosity of 330.0 cps (spindle #2 at 30 rpm at 25°C), a pH of 3.1, and a solids content of 25.3%.

#### Example 6

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To a resin reactor were charged 73.0 grams of the polyaminoamide resin of Example A, 61.2 grams of water, and 17.9 grams of the mono-chlorohydrin of Example F. The reactor contents were heated to 70°C and held at this temperature until the total alkalinity of the solution was about 60.89 mgKOH/gram. The polyaminoamide resin reaction product was diluted with 15.0 grams of water and cooled to about 50°C. Maleic anhydride in the amount of 8.1 grams

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was then added and allowed to react at about 80°C until a Brookfield viscosity of 2100 cps (spindle #2 at 12 rpm at 25°C) was obtained. After which, the resin solution was diluted with 144.0 grams of water, 225.7 grams of propylene glycol, and 15.3 grams of a 40% aqueous solution of polydiallydimethyammonium chloride, followed by adjusting the pH of the aqueous resin solution to 4.0 with 96% sulfuric acid. The resulting resin solution had a Brookfield viscosity of 110.0 cps (spindle #2 at 60 rpm at 25°C), a pH of 4.0, and a solids content of 12.0%.

# Comparative Example A (Resin without cationic polymer)

To a resin reactor were charged 116.4 grams of the polyaminoamide resin of Example A and 17.9 grams of the mono-chlorohydrin of Example E. The reactor contents were then heated to 80°C and held at this temperature until the total alkalinity of the solution was about 106.1 mg KOH/g. The polyaminoamide resin reaction product was then diluted with 101.7 grams of water and cooled to about 60°C. Maleic anhydride in the amount of 12.9 grams was then added and allowed to react at about 80°C until a Brookfield viscosity of 1863.cps (spindle #2 at 12 rpm at 25°C) was obtained. After which, 97.5 grams of water were added, followed by adjusting the pH of the aqueous resin solution to 4.0 with 96% sulfuric acid. The resulting resin solution had a 25 Prookfield viscosity of 296.0 cps (spindle #2 at 30 rpm at 25°C), a pH of 4.0, and a solids content of 24.9%.

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### Comparative Example B

Agefloc® PC-40, an antistatic agent based on a cationic polymer containing a polydiallyldimethylammonium chloride available from CPS Chemical Company.

## 5 <u>Testing of Product for Antistatic Effect</u>

The composition of Examples 1-6 and A and B were diluted with water to about 1% of solids. The pH of the solution was adjusted to about 7. Nylon 6,6 fabric was scoured by: (a) 10 minute immersion in 60 °C isopropanol; 10 (b) 20 minute immersion in 80 °C deionized water; (c) a second immersion in 80 °C deionized water; (d) air or oven dry; (e) cool to room temperature. The scoured nylon is immersed in the 1% solution of the examples for 20 sec. wrung, and air dried. The dried, treated fabric is cured 15 for approximately 3 sec at 180 °C. The cured samples are equilibrated overnight in a 47% relative humidity cabinet (27 °C). After equilibration the surface resistivity values are determined using a Milli-to-2 Wide Range Resistance Meter with an Electro-Tech Systems, Inc., Model 20 803A, surface/volume resistivity probe. The treated substrates were then subjected to multiple washings, etc., which would typically result in the extraction of the antistatic composition. Resistivity were then again performed, per the above method, to determine the 25 permanence of the antistatic composition after the abovedescribed subsequent treatments. The surface resistance data are reported as the base 10 logarithm of the surface

resistance measured in ohms. In these tests, increases in Log (R) value of approximately 1.0 Log (R) units, or less, after the washing process show satisfactory permanence of the anti-static composition. Initial and subsequent resistivity results are shown in Table I below.

Table I

1.5	·		and the second s
	T	Initial (Log R)	Log R after immersion
	blank	14.30	14.30
•	1	11.70	12.70
10	2	11.85	12.70
	3	10.47	11.49
	4 .	9.80	10.40
	5	9.80	10.70
	6	10.70	11.70
15	Comp. A	11.10	14.00
٠,	Comp. B	11.40	14.00

As can be seen from the results obtained in Table I, an antistatic composition in accodance with the present invention is significantly more permanent, as compared to those known in the art. Those polymeric substrates treated with the disclosed antistatic composition provide adequate static electricity dissipating properties even after they are subjected to various treatment steps which would normally cause the antistatic composition to be extracted from the polymeric textile substrate.

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What is claimed is:

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## 1. A composition comprising:

- (a) a crosslinked thermosetting resin formed by reacting, in the presence of a water-soluble solvent, a polyaminoamide having unreacted primary and secondary amine groups and an anhydride selected from the group consisting of dianhydride, maleic anhydride, and mixtures thereof; and
  - (b) a cationic polymer.
- 2. The composition of claim 1 wherein said unreacted primary and secondary amine groups of said polyaminoamide are reacted with said anhydride in a mole ratio of anhydride:unreacted amine groups of from about 0.1:1.0, respectively.
- 3. The composition of claim 1 wherein said crosslinked thermosetting resin is present at a concentration of from about 0.1 to about 60% by weight, based on the weight of said resin.
  - 4. The composition of claim 3 wherein said crosslinked thermosetting resin is present at a concentration of about 35% by weight, based on the weight of said resin.
  - 5. The composition of claim 1 wherein said anhydride is dianhydride.
  - 6. The composition of claim 1 wherein said anhydride is maleic anhydride.
- 7. The composition of claim 1 wherein up to about 10% by weight of said unreacted primary and secondary amine groups of said polyaminoamide are reacted with mono-chlorohydrin

derivatives of  $C_{6-20}$  fatty alkoxylates.

8. The composition of claim 7 wherein said  $C_{6-20}$  fatty alkoxylates contain from at least 1 up to about 200 moles of an alkoxylate selected from the group consisting of ethylene oxide, propylene oxide, and mixtures thereof, said alkoxylate being reacted with a  $C_{6-20}$  fatty alcohol.

- 9. The composition of claim 8 wherein said alkoxylate has a ratio of ethylene oxide:propylene oxide in the range of about 25: 1 to about 4:1, respectively.
  - 10 10. The composition of claim 7 wherein said monochlorohydrin derivatives are prepared by reacting epichlorohydrin with an alkoxylated fatty alcohol in equimolar ratios using a boron trifluoride catalyst.
  - 11. The composition of claim 1 wherein said crosslinked thermosetting resin has a viscosity at about 35% solids of at least 300 cps at 25°C.
    - 12. The composition of claim 1 wherein said crosslinked thermosetting resin has a pH of less than 9.
  - 13. The composition of claim 1 containing from about 1 to
    20 about 25% by weight of said cationic polymer, based on the
    weight of said crosslinked thermosetting resin.
    - 14. The composition of claim 1 wherein said cationic polymer is polydiallyldimethylammonium chloride.
  - 15. The composition of claim 1 wherein said solvent is water.
- 16. A process for producing an antistatic composition comprising the steps of:
  - (a) forming a polyaminoamide having unreacted primary

and secondary amine groups;

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(b) reacting, in the presence of a water-soluble solvent, said polyaminoamide with an anhydride selected from the group consisting of dianhydride, maleic anhydride, and mixtures thereof, to form a crosslinked thermosetting resin; and

- (c) blending said crosslinked thermosetting resin with a cationic polymer.
- 17. The process of claim 16 wherein said unreacted primary

  10 and secondary amine groups of said polyaminoamide are
  reacted with said anhydride in a mole ratio of
  anhydride:unreacted amine groups of from about 0.1:1.0,
  respectively.
- 18. The process of claim 16 wherein said crosslinked

  thermosetting resin is formed at a concentration of from about 0.1 to about 60% by weight, based on the weight of said resin.
  - 19. The process of claim 18 wherein said crosslinked thermosetting resin is formed at a concentration of about 35% by weight, based on the weight of said resin.
  - 20. The process of claim 16 wherein said anhydride is dianhydride.
  - 21. The process of claim 16 wherein said anhydride is maleic anhydride.
- 25 22. The process of claim 16 wherein up to about 10% by weight of said unreacted primary and secondary amine groups of said polyaminoamide are reacted with mono-chlorohydrin derivatives of  $C_{6-20}$  fatty alkoxylates.

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23. The process of claim 22 wherein said  $C_{6-20}$  fatty alkoxylates contain from at least 1 up to about 200 moles of an alkoxylate selected from the group consisting of ethylene oxide, propylene oxide, and mixtures thereof, said alkoxylate being reacted with a  $C_{6-20}$  fatty alcohol.

- 24. The process of claim 23 wherein said alkoxylate has a ratio of ethylene oxide:propylene oxide in the range of about 25 : 1 to about 4:1, respectively.
  - 25. The process of claim 22 wherein said mono-chlorohydrin 10 derivatives are prepared by reacting epichlorohydrin with an alkoxylated fatty alcohol in equimolar ratios using a boron trifluoride catalyst.
    - 26. The process of claim 16 wherein said crosslinked thermosetting resin has a viscosity at about 35% solids of at least 300 cps at 25°C.
      - The process of claim 16 wherein said crosslinked thermosetting resin has a pH of less than 9.
      - The process of claim 16 wherein from about 1 to about 25% by weight of said cationic polymer, based on the weight
- 20 of said crosslinked thermosetting resin, is blended into said crosslinked thermosetting resin.
  - 29. The process of claim 16 wherein said cationic polymer is polydiallyldimethylammonium chloride.
- The process of claim 16 wherein said water-soluble 25 solvent is water.
- The process of claim 16 wherein said polyaminoamide is formed by reacting a polyamine and a polyacid.
- 32. The process of claim 16 wherein said step (b) is

conducted at a temperature of from about 25 to 100°C.

33. A process for dissipating an electrostatic charge on a static-prone natural and synthetic polymeric substrate comprising contacting said substrate with an antistatic composition containing:

- (a) a crosslinked thermosetting resin formed by reacting, in the presence of a water-soluble solvent, a polyaminoamide having unreacted primary and secondary amine groups and an anhydride selected from the group consisting of dianhydride, maleic anhydride, and mixtures thereof; and
  - (b) a cationic polymer.

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- 34. The process of claim 33 wherein said unreacted primary and secondary amine groups of said polyaminoamide are reacted with said anhydride in a mole ratio of anhydride:unreacted amine groups of from about 0.1:1.0, respectively.
  - 35. The process of claim 33 wherein said crosslinked thermosetting resin is present at a concentration of from about 0.1 to about 60% by weight, based on the weight of said resin.
  - 36. The process of claim 35 wherein said crosslinked thermosetting resin is present at a concentration of about 35% by weight, based on the weight of said resin.
- 37. The process of claim 33 wherein said anhydride is dianhydride.
  - 38. The process of claim 33 wherein said anhydride is maleic anhydride.
    - 39. The process of claim 33 wherein up to about 10% by

weight of said unreacted primary and secondary amine groups of said polyaminoamide are reacted with mono-chlorohydrin derivatives of  $C_{6-20}$  fatty alkoxylates.

- 40. The process of claim 39 wherein said  $C_{6-20}$  fatty alkoxylates contain from at least 1 up to about 200 moles of an alkoxylate selected from the group consisting of ethylene oxide, propylene oxide, and mixtures thereof, said alkoxylate being reacted with a  $C_{6-20}$  fatty alcohol.
  - 41. The process of claim 40 wherein said alkoxylate has a ratio of ethylene oxide:propylene oxide in the range of about 25 : 1 to about 4:1, respectively.
    - 42. The process of claim 39 wherein said mono-chlorohydrin derivatives are prepared by reacting epichlorohydrin with an alkoxylated fatty alcohol in equimolar ratios using a boron trifluoride catalyst.
    - 43. The process of claim 33 wherein said crosslinked thermosetting resin has a viscosity at about 35% solids of at least 300 cps at 25°C.
  - 44. The process of claim 33 wherein said crosslinked thermosetting resin has a pH of less than 9.

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- 45. The process of claim 33 containing from about 1 to about 25% by weight of said cationic polymer, based on the weight of said crosslinked thermosetting resin.
- 46. The process of claim 33 wherein said cationic polymer is polydiallyldimethylammonium chloride.
  - 47. The process of claim 33 wherein said solvent is water.
  - 48. A process for dissipating an electrostatic charge on a static-prone natural or synthetic article of manufacture

comprising the steps of:

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(1) providing a hot melt natural or synthetic polymeric substrate used to form an article of manufacture;

- (2) blending said hot melt polymeric substrate with an antistatic composition, said antistatic composition containing:
  - (a) a crosslinked thermosetting resin formed by reacting, in the presence of a water-soluble solvent, a polyaminoamide having unreacted primary and secondary amine groups and an anhydride selected from the group consisting of dianhydride, maleic anhydride, and mixtures thereof; and (b) a cationic polymer, thus forming a blended
    - (3) cooling said blended hot melt polymeric substrate.

hot melt polymeric substrate; and

to form an article of manufacture.

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- 49. The process of claim 48 wherein from about 0.1 to about 10% by weight, based on the weight of said hot melt polymeric substrate, of said antistatic composition is blended with said hot melt polymeric substrate.
- 50. The process of claim 48 wherein said unreacted primary and secondary amine groups of said polyaminoamide are reacted with said anhydride in a mole ratio of anhydride:unreacted amine groups of from about 0.1:1.0, respectively.

# INTERNATIONAL SEARCH REPORT

International application No. PCT/US96/12772

A. CLASSIFICATION OF SUBJECT MATTER  IPC(6) :C08L 77/12; C08F 283/04; C08G 69/44; C08J 5/00  INC. CO. CO. CO. CO. CO. CO. CO. CO. CO. C	.								
US CL: 524/539; 525/423, 426, 430, 63, 178; 427/374.1, 384 According to International Patent Classification (IPC) or to both national classification and IPC	1								
B. FIELDS SEARCHED									
Minimum documentation searched (classification system followed by classification symbols)									
U.S. : 524/539; 525/423, 426, 430, 63, 178; 427/374.1, 384									
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched	4								
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)									
C. DOCUMENTS CONSIDERED TO BE RELEVANT									
Category* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim	n No.								
Y US, A, 4,172,887 (VANLERBERGHE ET AL) 30 October 1-50 1979, see entire document	·								
Y US, A, 3,912,808 (SOKOL) 14 October 1975, see entire document 1-50									
Further documents are listed in the continuation of Box C. See patent family annex.									
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<ul> <li>Special categories of cited documents:</li> <li>A* document defining the general state of the art which is not considered</li> <li>Inter document published after the international filing date or determined in conflict with the application but cited to underst principle or theory underlying the invention</li> </ul>	and the								
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*O* document referring to an oral disclosure, use, exhibition or other combined with one or more other such documents, such combined with one or more other such documents, such combined with one or more other such documents, such combined with one or more other such documents, such combined with one or more other such documents.	oinstian.								
*p* document published prior to the international filing date but later than *&* document member of the same patent family the priority date claimed	<del></del>								
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Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231  Authorized officer MARGARET GLASS									
Facsimile No. (703) 305 3239 Telephone No. (703) 308-2351	<u></u>								